

## REFLECTANCE AND LUMINESCENCE SPECTRA OF CaS:Pr PHOSPHORS

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Reflectance spectra and photoluminescence from the ultraviolet (UV) to the near infrared (NIR) have been studied for CaS:Pr phosphors of different concentrations. The absolute intensities of eight bands between UV and NIR have been measured. These bands result from forced electric-dipole transitions between the  $^3H_4$  ground manifold and various excited  $J$  manifolds of the  $Pr^{3+}$  ion. The transition intensities have been accounted for in terms of three phenomenological parameters with an rms error of 6-10%. By applying the Judd-Ofelt theory and by using the photoluminescence spectral patterns, the spontaneous emission probabilities and relaxation rates of fluorescent states have been determined. The measured fluorescence lifetimes of the  $^1D_2 \rightarrow ^3H_4$  transition of CaS:Pr (0.5 and 1.0 M%) are in good agreement with the theoretical values. The emission cross sections for the fluorescent states of  $^3P_1 \rightarrow ^3F_3$ ,  $^3P_0 \rightarrow ^3F_2$  have been measured by using the Judd-Ofelt technique.

## 1. Introduction

Alkaline-earth chalcogenides are known to be highly efficient phosphor materials [1,2]. Recently, detailed studies of the lasing properties of  $Nd^{3+}$  and  $Tb^{3+}$  have been reported [3,4] and laser selective excitation of CaS:Pr phosphor has been carried out [5]. There has been renewed interest in CaS phosphors doped with rare earths, because of their high luminescence efficiency. A fast and simple method of preparing such phosphors is described in the present work.

This paper also reports the results of spectroscopic properties such as reflectance, excitation, photoluminescence and lifetime measurements for the luminescence states of CaS:Pr phosphors, both at room temperature and at liquid-nitrogen temperature.

## 2. Experimental procedures

## 2.1. Material preparation

Praesodymium activated calcium sulphide phosphors were prepared with different concentration 0.2, 0.5, 1.0 and 1.5 M% (M/M CaS). A mixture of  $Pr_6O_{11}$  (99.9%), CaO or  $CaCO_3$  (99.95%) was ground thoroughly and then reduced with sulphur in a quartz tube which was pumped to  $10^{-2}$  Torr at a temperature of 950-1000°C for 30 min in order to remove the absorbed sulphur in the powder phosphors. The samples were annealed at much lower temperatures than previously reported in the literature in a flowing stream of  $N_2$  or Ar for 20 min. X-ray powder diffraction patterns confirmed that all the samples are rock salt lattice CaS.

## 2.2. Measurements

The reflectance spectra at room temperature of the

CaS:Pr phosphor  
SP 720 spectro  
Freshly prepare  
reference sample.  
combusting the  
for each of the  
work. The refle  
room temperat  
Photolumine  
were measured  
rophotometer  
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ratus was used  
400 nm wavele  
length used be  
and excitation  
77 K.

The lifetime  
be 32  $\mu$ s at roo  
both the 1.0  
having the sar  
an NRGO 9-5  
excitation wa  
grating mono  
a Hamamatsu  
were recorded

## 3. Results and

## 3.1. Reflectance

## 3.1.1. Energy

Eight energy  
positions of  
CaS:Pr phosphor  
compared with  
least-squares  
energy level ( $E^1, E^2, E^3$ )  
error  $\delta_{rms}$  parameters are

## 3.1.2. Bonding

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earlier by Ift  
evaluated in  
(table 1) of  
CaS:Pr phosphor

CaS:Pr phosphors were measured with a UNICAM SP 720 spectrophotometer from 200 to 3000 nm. Freshly prepared MgO powder was used as the reference sample. The MgO powder was obtained by combusting the magnesium metal in the atmosphere for each of the four samples studied in the present work. The reflectance spectra were recorded only at room temperature.

Photoluminescence emission spectra of CaS:Pr were measured with a Hitachi MPF-4 spectrofluorophotometer from 400 to 760 nm with a 280 nm xenon lamp as excitation source. The same apparatus was used to obtain excitation spectra in the 240–400 nm wavelength region with the monitored wavelength used being 665 nm. The photoluminescence and excitation spectra were recorded both at 300 and 77 K.

The lifetime of the  $\text{Pr}^{3+}$  excited state was found to be 32  $\mu\text{s}$  at room temperature and 36  $\mu\text{s}$  at 77 K, with both the 1.0 M% and the 0.5 M% concentrations having the same lifetime. The excitation source was an NRG O 9-5-30 nitrogen laser and 337 nm was the excitation wavelength used. An SPX 1403 double-grating monochromator spectrometer was used with a Hamamatsu R-938 photomultiplier and the signals were recorded by a PARC 162/165 boxcar.

### 3. Results and discussion

#### 3.1. Reflectance spectra

##### 3.1.1. Energy levels

Eight energy levels were measured from the peak positions of the recorded reflectance spectra of CaS:Pr phosphors. The measured energies have been compared with theoretical energies by employing a least-squares fit method. The energies, along with the energy level characteristic parameters, namely Racah ( $E^1, E^2, E^3$ ), spin-orbit ( $\zeta_{4f}$ ) and the rms deviation error  $\delta_{\text{rms}}$  parameter are presented in table 1. The mathematical procedures used to calculate these parameters are already available in the literature [6,7].

##### 3.1.2. Bonding

Following the theoretical considerations reported earlier by Iftikar [8] and Legendziewics [9], we have evaluated the bonding parameter ( $\delta$ ). Our results (table 1) confirm the ionic bonding nature of the CaS:Pr phosphors.

#### 3.2. Absolute intensities

Between the visible and the near-infrared regions the recorded reflectance spectra of CaS:Pr phosphors show typically eight absorption levels which originate from the  $^3\text{H}_4$  ground state.

The basis of the present studies is the theory for crystal-field-induced electric-dipole transitions between 4f states which has been developed by Judd and Ofelt [10,11] for the trivalent rare earths. In this section are presented the relevant aspects of the Judd-Ofelt model.

The electric-dipole transition line strengths between an initial  $J$  manifold ( $SLJ$ ) and a final  $J$  manifold ( $S'L'J'$ ) are given as [12]

$$S = \sum_{\lambda=2}^6 \Omega_{\lambda} \langle (SLJ) \| U^{\lambda} \| S'L'J' \rangle^2,$$

where the three terms  $\| U^{\lambda} \|^2$  are the doubly reduced unit tensor operators observed in the intermediate-coupling approximation, and the coefficients contain the effects of the odd-symmetry crystal-field terms, radial integrals and energy denominators. The unit tensor operators have been computed numerically using the Racah and spin-orbit parameters (table 1) by solving the  $4f^2$  energy matrices.

The line strength ( $S$ ) is related to the integrated absorbance of an electric-dipole transition [13] by

$$\int K(\lambda) d\lambda = \frac{8\pi^3 e^2 \lambda N}{3ch(2J+1)n} \frac{1}{9} \frac{(n^2+2)^2}{9} S,$$

where  $K(\lambda)$  is the absorption coefficient at  $\lambda$ ,  $N$  is the concentration of  $\text{Pr}^{3+}$  (ions  $\text{cm}^{-3}$ ),  $J$  is the angular momentum of the initial level (which for  $\text{Pr}^{3+}$  is  $^3\text{H}_4$ ),  $n$  is the refractive index and  $(n^2+2)^2/9$  is the local field.

The spectrophotometric tracings were taken for a given CaS:Pr phosphor concentration and the various observed bands were integrated. A computerised least-squares fitting routine from the measured spectral intensities, determines the best-fit phenomenological parameters ( $\Omega_2, \Omega_4, \Omega_6$ ). Both the measured and theoretical spectral intensities of the eight observed bands are listed in table 2. The quality of the fit can be expressed by the rms error parameter. Examination of the data in table 2, supports the suitability of the Judd-Ofelt model for determining the oscillator strengths. The deviation parameter  $\delta_{\text{rms}}$  is obtained from [14]

Table 1  
The measured and computed absorption energies (cm<sup>-1</sup>) and the energy level parameters of CaS:Pr phosphors

Absorption state from <sup>3</sup> H <sub>4</sub>	1.5 M%		1.0 M%		0.5 M%		0.2 M%	
	E <sub>expt</sub>	E <sub>cal</sub>	E <sub>expt</sub>	E <sub>cal</sub>	E <sub>expt</sub>	E <sub>cal</sub>	E <sub>expt</sub>	E <sub>cal</sub>
<sup>3</sup> P <sub>2</sub>	23300	23313	23180	23257	23060	23142	-	23096
<sup>3</sup> P <sub>1</sub>	22050	22028	22000	21988	21870	21903	-	21875
<sup>3</sup> P <sub>0</sub>	21400	21360	21310	21325	21295	21251	-	21228
<sup>1</sup> D <sub>2</sub>	17300	17280	17200	17181	17100	17039	-	16931
<sup>1</sup> G <sub>4</sub>	9890	9876	9880	9833	9800	9751	9700	9694
<sup>3</sup> F <sub>4</sub>	6870	6832	6850	6811	6780	6770	6780	6741
<sup>3</sup> F <sub>3</sub>	6500	6472	6385	6450	6370	6404	6320	6385
<sup>3</sup> F <sub>2</sub>	5120	5084	5100	5168	5100	5050	5100	5042
δ <sub>rms</sub>	± 36		± 56		± 65		± 67	
E <sup>1</sup> (cm <sup>-1</sup> )	4655.41		4632.76		4606.32		4574.09	
E <sup>2</sup> (cm <sup>-1</sup> )	22.66		22.51		22.29		22.17	
E <sup>3</sup> (cm <sup>-1</sup> )	471.38		470.84		469.67		469.40	
ζ <sub>4f</sub> (cm <sup>-1</sup> )	789.66		783.96		771.99		766.32	
B <sub>6</sub>	1.0221		1.0177		1.0118		1.0073	
δ	-0.0216		-0.0174		-0.0116		-0.0072	

$$\delta_{rms} = \left( \sum \frac{(f_m - f_c)^2}{N - P} \right)^{1/2}$$

where N is the number of levels used in the fitting and P represents the freely varying parameters (JO parameters). Among these three Judd-Ofelt parameters (table 2), the following order of magnitude is observed

$$\Omega_2 > \Omega_6 > \Omega_4$$

which shows that Ω<sub>2</sub> is the most sensitive parameter to characterize the spectral intensities.

### 3.3. Hypersensitive transition

A few of the 4f-4f transitions are found to be very

Table 2  
Absorption intensities (f<sub>m</sub> × 10<sup>6</sup>; f<sub>c</sub> × 10<sup>6</sup>) and Judd-Ofelt intensity parameters of CaS:Pr phosphors

Absorption state from <sup>3</sup> H <sub>4</sub>	1.5 M%		1.0 M%		0.5 M%		0.2 M%	
	f <sub>m</sub>	f <sub>c</sub>	f <sub>m</sub>	f <sub>c</sub>	f <sub>m</sub>	f <sub>c</sub>	f <sub>m</sub>	f <sub>c</sub>
<sup>3</sup> P <sub>2</sub>	9.60	10.12	7.30	7.13	5.18	4.95	-	2.75
<sup>3</sup> P <sub>1</sub>	4.40	4.62	3.25	3.03	2.60	2.39	-	1.11
<sup>3</sup> P <sub>0</sub>	4.15	4.40	3.10	2.97	2.50	2.35	-	1.09
<sup>1</sup> D <sub>2</sub>	3.20	4.48	2.35	2.24	1.45	1.53	-	0.85
<sup>1</sup> G <sub>4</sub>	0.90	0.91	0.70	0.69	0.39	0.44	0.18	0.24
<sup>3</sup> F <sub>4</sub>	10.20	10.71	7.32	7.54	5.30	5.12	2.26	2.90
<sup>3</sup> F <sub>3</sub>	17.20	18.06	12.30	12.72	6.20	6.66	3.95	3.82
<sup>3</sup> F <sub>2</sub>	17.90	18.79	13.00	13.23	8.20	7.72	4.85	4.67
δ <sub>rms</sub>	± 0.60		± 0.27		± 0.35		± 0.68	
Ω <sub>2</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	21.11		14.87		8.26		5.31	
Ω <sub>4</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	4.24		2.99		2.37		1.10	
Ω <sub>6</sub> (10 <sup>-20</sup> cm <sup>2</sup> )	10.75		7.57		5.21		2.96	

sensitive to the F transitions exhibiting are called the hyperintense transition <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> satisfies selection rules. The spectral oscillations are more intense than those of the transition studied. It is a function of the intensity of this band. The parameter, as is

### 3.4. Photoluminescence

The measured photoluminescence intensities of various photoluminescence transitions are given in table 3. The experimental and theoretical Judd-Ofelt intensities are compared. In the following, the following phosphors have been studied: Property (i). The intensity from an initial state (S' L' J') has

$$I(s^{-1}) = \frac{64\pi^4 e^2}{3h(2J)}$$

Table 3  
The measured and ca

sensitive to the  $\text{Pr}^{3+}$  concentration [15,16]. These transitions exhibit peculiar intensity variations and are called the hypersensitive levels. For  $\text{Pr}^{3+}$ , the transition  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$  is the hypersensitive level, which satisfies selection rules such as  $\Delta J$  and  $\Delta L=2, \Delta S \geq 0$ . The spectral oscillator strength of this transition is more intense than the other remaining states of the ion studied. It is very significant that the spectral intensity of this band is strongly monitored by the  $\Omega_2$  parameter, as is seen from table 2.

3.4. Photoluminescence spectra

The measured and computed energies of the various photoluminescent states of CaS:Pr phosphors are given in table 3. A good agreement between theory and experiment has been obtained. With the Judd-Ofelt intensity parameters, as explained earlier, the following radiative properties of CaS:Pr phosphors have been determined.

Property (i). The spontaneous emission probability from an initial manifold ( $SLJ$ ) to a final manifold ( $S'L'J'$ ) has been computed from [17]

$$A(s^{-1}) = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} n \frac{(n^2+2)^2}{9} S.$$

Property (ii). The fluorescent branching ratio ( $\beta_{JJ'}$ ) for a transition from ( $SLJ$ )  $\rightarrow$  ( $S'L'J'$ ) is given by [17]

$$\beta_{JJ'} = A / \sum A,$$

where the sum is over all possible terminal manifolds.

Property (iii). The radiative lifetime is obtained from (17)

$$T_R(\mu s) = [A_T]^{-1}.$$

Table 4 describes the values of the spontaneous emission probability  $A(s^{-1})$ , the measured (both at 300 and 77 K) and computed lifetime values for the fluorescent transition  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_5$  of the CaS:Pr phosphors. The experimental lifetimes are in excellent agreement with the theoretical values.

Property (iv). For the two observed luminescence transitions, namely  ${}^3\text{P}_1 \rightarrow {}^3\text{F}_3$  and  ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ , the induced-emission cross section  $\sigma_p$  ( $10^{-20} \text{ cm}^2$ ) has been measured using the expression [18]

$$\sigma_p = \frac{\lambda^4}{8\pi c n^2 \Delta\lambda} A,$$

where  $\lambda$  is the luminescent state wavelength (nm) and  $\Delta\lambda$  is the bandwidth, which has been determined

Table 3  
The measured and calculated energies of the photoluminescent states of CaS:Pr phosphors

Fluorescent transition	0.5 M%		1.0 M%	
	$E_{\text{meas.}}$ ( $\text{cm}^{-1}$ )	$E_{\text{theo.}}$ ( $\text{cm}^{-1}$ )	$E_{\text{meas.}}$ ( $\text{cm}^{-1}$ )	$E_{\text{theo.}}$ ( $\text{cm}^{-1}$ )
${}^3\text{P}_1 \rightarrow {}^3\text{F}_4$ $\rightarrow {}^3\text{F}_3$ $\rightarrow {}^3\text{F}_2$ $\rightarrow {}^3\text{H}_6$ $\rightarrow {}^3\text{H}_5$	15133	15152	15220	15200
	15499	15508	15565	15550
	16953	16961	17075	17050
	17465	17488	17600	17570
	19725	19732	19850	19820
${}^3\text{P}_0 \rightarrow {}^3\text{F}_4$ $\rightarrow {}^3\text{F}_3$ $\rightarrow {}^3\text{F}_2$ $\rightarrow {}^3\text{H}_6$ $\rightarrow {}^3\text{H}_5$	14481	14505	14610	14590
	14847	14861	14960	14950
	16301	16304	16420	16415
	16813	16842	16920	16905
	19073	19085	19190	19180
${}^1\text{D}_2 \rightarrow {}^3\text{H}_5$ $\rightarrow {}^3\text{H}_4$	14961	14989	15105	15100
	17039	17060	17115	17100

Table 4  
The measured and calculated lifetimes of the fluorescent transition  $^1D_2 \rightarrow ^3H_5$  (663.5 nm) of CaS:Pr phosphors

Radiative properties	1.5 M%	1.0 M%	0.5 M%	0.2 M%
$A(s^{-1})$	46.06	32.43	29.12	15.76
$T_R(\mu s)$	21.71	30.83	34.32	65.53
$T_i(\mu s)$ (300 K)		32.0	32.0	
$T_i(\mu s)$ ( 77 K)		36.0	36.0	

by integrating the band shape and dividing by the intensity (relative) at  $\lambda$ ,  $c$  is the velocity of light,  $n$  is the refractive index of the phosphor and  $A$  is the transition probability.

The measured stimulated emission cross section  $\sigma_p$  ( $10^{-20}$  cm $^2$ ), transition probability  $A(s^{-1})$  and branching ratio ( $\beta_{JJ'}$ ) values of the fluorescent laser transitions  $^3P_1 \rightarrow ^3F_3$  and  $^3P_0 \rightarrow ^3F_2$  (645 and 613 nm respectively) of CaS:Pr phosphors are presented in table 5. From the results illustrated in tables 1-5, we have drawn the following conclusions.

#### 4. Conclusions

Reflectance spectra, excitation spectra and photoluminescence spectra of CaS:Pr phosphors have been investigated and the energy level structure of these phosphors has been characterised by the energy level parameters. The magnitudes of the bonding parameters ( $B_k, \delta$ ) demonstrated the ionic nature of the CaS:Pr phosphors in all four concentrations.

Application of the Judd-Ofelt theory has resulted in the achievement of a good fitting of reflectance

spectral intensities of f-f transitions with high accuracy through the estimation of electric-dipole line strengths.

The interesting influences of the  $Pr^{3+}$  ion concentration on the spectral intensities, as shown by the hypersensitive transition ( $^3H_4 \rightarrow ^3F_2$ ), have also been studied and have been found to be significantly monitored by the  $\Omega_2$  parameter.

By the use of Judd-Ofelt theory, the radiative properties of CaS:Pr phosphors were determined. The lifetimes of the  $^1D_2 \rightarrow ^3H_5$  transition of CaS:Pr at 300 and 77 K were measured by using a  $N_2$  laser to excite the phosphor and these experimental values were correlated with the theoretical lifetimes obtained through the Judd-Ofelt technique. The results presented in table 4 demonstrate that the Judd-Ofelt model can be successfully applied to the phosphors in correlating the measured and computed lifetimes of the fluorescent state. The agreement between the calculated and measured lifetimes was better than 6%. This technique permits a relatively rapid determination of radiative lifetimes, branching ratios, and induced-emission cross sections and was thoroughly utilized in the present work to investigate the systematic dependence of the properties with rare-earth

Table 5  
The measured induced-emission cross section  $\sigma_p$  ( $10^{-20}$  cm $^2$ ) for the fluorescent laser levels ( $^3P_1 \rightarrow ^3F_3$ ;  $^3P_0 \rightarrow ^3F_2$ ) of CaS:Pr phosphors

Transition	Parameters	0.5 M%	1.0 M%
$^3P_1 \rightarrow ^3F_3$	$\sigma_p$ ( $10^{-20}$ cm $^2$ )	2.13	3.79
	$A$ ( $s^{-1}$ )	47574.0	84018.0
	$\beta_{JJ'}$	0.392	0.431
$^3P_0 \rightarrow ^3F_2$	$\sigma_p$ ( $10^{-20}$ cm $^2$ )	3.14	5.63
	$A$ ( $s^{-1}$ )	77854.0	139094.0
	$\beta_{JJ'}$	0.612	0.683

ion concentration of the Judd-Ofelt theory with fluorescent transition cross sections  $^3P_1 \rightarrow ^3F_3$  and  $^3P_0 \rightarrow ^3F_2$  measured induced-emission cross sections of these two transitions.

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ion concentration in the CaS phosphor. Combination of the Judd-Ofelt theory of electric-dipole transitions with fluorescence line shapes provided a convenient way to determine the stimulated-emission cross sections of the fluorescent levels such as  ${}^3P_1 \rightarrow {}^3F_3$  and  ${}^3P_0 \rightarrow {}^3F_2$  in the CaS:Pr phosphors. The measured induced-emission cross section values of these two transitions are given in table 5.

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